Composites Part B 178 (2019) 107488

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Piezoresistive behaviours of cement-based sensor with carbon black subjected to various temperature and water content

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ARTICLE INFO

Keywords:
Carbon black
Cement-based sensor
Fractional changes of resistivity
Temperature
Water content

ABSTRACT

Cement-based sensor possesses unique properties for structural health monitoring (SHM) applications, such as low cost, high durability, adaptability and excellent sensitivity. The piezoresistivity of cement-based sensor possesses is often affected by working environments, which may limit its real potentials. In this study, the piezoresistive sensitivity and repeatability of cement-based sensors with carbon black (CB) under various environmental conditions were investigated. Under various temperatures ranging from $-20\,^{\circ}$C to $100\,^{\circ}$C, the piezoresistive sensitivity and repeatability were almost unchanged when eliminating the effects by thermal exchanges. The water content of cementitious composites caused significant fluctuations on the resistivity and piezoresistivity, and the optimal water content for cement-based sensor possesses was found to be approximately 8%. Subjected to freeze-thaw cycles, dry CB/cementitious composites slightly reduced the piezoresistive sensitivity. However, the saturated composites presented dramatic piezoresistivity reduction by 30.7%, due to the microstructural damages caused by the volume expansion and shrinkage of pore solution. The related outcomes provide scientific framework for the adoption of CB/cementitious composites sensors for the SHM of concrete infrastructures under various environmental conditions.

1. Introduction

Conductive fillers reinforced composites for concrete structural health monitoring (SHM) have attracted much more attentions from both engineers and scientists [1–7], particularly the high durability, sensitivity, accuracy and economic efficiency for the conductive nanomaterials reinforced cementitious composites. Compared to conventional sensors of strain gauge, optic fibre, piezoelectric ceramic, piezoresistive cement-based sensor has many advantages including its simple manufacturing and installation, high strength and durability, and the highly sensitive and self-sensing ability [8–22]. Piezoresistivity of cement-based composites, which represents electrical resistivity changes with external forces, comes from the relative positions between filled conductive particles/fibres, the pore solutions and electrically insulated cement hydration products and pore airs [23–26]. Generally, the relative locations of conductive and non-conductive constitutes in the cementitious composites could be altered in accordance with external forces, and then the changed resistivity could be recorded automatically and transformed to the values of forces, or deformations. Currently investigations have proved that the piezoresistive cement-based composites could successfully monitor the deformation and damage of concrete structures with hundreds of times higher efficiency compare to commercial strain gauge [27–30].

However, the monitored cement-based sensors are always subject to a wide range of working temperature and humidity from the extremely cold and dry weather, high temperature areas, to the regions with huge temperature differences during day and night alternations, such as deserts or oceans. Combined with the concrete for special purpose such as furnace, pipelines, heat-resistant characteristics for important structures or dams, it becomes a challenge for the operation of piezoresistive based cementitious sensors in the extreme conditions without any disturbance. It is believed that the resistivity of composite can vary significantly with temperature and humidity, let alone their influences on piezoresistivity [23]. Moreover, the effects of working environments such as temperature, water content and freeze-thaw cycles on the piezoresistive-based cement sensor have rarely been investigated, with a few studies mainly focusing on the effect of water content [31–34].

Previous studies [35–37] observed decreased resistivity of carbon fibre assisted cement-based composite with increased temperature, but none finds the alterations under different freeze-thaw cycles. By

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https://doi.org/10.1016/j.compositesb.2019.107488
Received 26 June 2019; Received in revised form 25 September 2019; Accepted 27 September 2019
Available online 29 September 2019

investigating the electrical resistivity of cement mortar under freeze-thaw cycles with/without freezing process, Cao and Chung [38] proposed that the thermal cycles without freezing produced no differences on the resistivity due to the undamaged microstructures. However, their experimental specimen was plain cement mortar, rather than the conductors reinforced conductive cement composite. Also, none of above studies has involved the dependence of piezoresistivity of cementitious composites on different temperatures. Furthermore, Wang et al. [39] studied the effect by 200 freeze-thaw cycles of −10 °C–10 °C, and −20 °C–20 °C with NaCl solution, and found that the piezoresistivity of CNF embedded cement sensor was deteriorated with freeze-thaw cycles. However, because of the combination of both freeze-thaw cycles and salt solutions, the specific impacts caused by one or another were still ambiguous and difficult to determine.

Environmental humidity has strong effect on resistivity and piezoresistivity of cement-based sensors, which is mainly due to its contributions on the cementitious composite water content, pore solutions and cement hydration. Previous studies proved that the improved conductivity by external humidity primarily came from the moisture layers in micro pores or cracks [40]. Some studies also found that the conductors filled cement composites have better resistance to humidity changes on conductivity in comparison to the counterpart without fillers [36]. However, improved electrical conductivity caused by water content has limited relationship to the piezoresistivity. Wen et al. [41] explored the carbon fibre added cement paste in saturated states, and proposed that the resistivity was decreased compared to that in dry state, as well as the decreased piezoresistivity. Similarly, the hybrid fillers of CB, carbon nanotubes and carbon fibres reinforced cementitious composites were investigated by Hong et al. [42], and a continually reduced fractional changes of resistivity (*FCR*) with increased saturation degree was observed. However, opposite conclusions were represented by Zhang et al. [31] who observed a weakened self-sensing ability with the decease of water content. Furthermore, Han et al. [32] investigated the Multi-walled carbon nanotubes (MWCNTs) reinforced cement sensor under different degrees of drying, and they found that the piezoresistive sensitivity increased first then decreased with increase of water content. But still, previous investigations either ignored the situation of high water content to saturation, or the resistivity and piezoresistivity performances under external forces.

Therefore, in this study, to obtain the environmental behaviours of CB cementitious composites, temperatures from −20 °C to 100 °C and relative humidity from totally dry to fully saturation were applied for the CB filled cement-based sensor, to explore their impacts on the electrical resistivity and piezoresistivity of the cement-based sensors. The electrical resistivity and piezoresistive performance of CB cementitious sensors before and after the freeze-thaw cycles were also investigated and compared to assess the piezoresistive sensitivity reduction in changeable working environments. CB is much cheaper than that of other widely used conductive nanomaterials such as MWCNTs or carbon nanofibers, which is the reason for choosing it for cement-based sensor production in this study. The related results will provide a strong insight into the real application of CB filled cement-based sensors for concrete infrastructures under circumstances with various climate changes and humidity conditions.

2. Experimental program

2.1. Raw materials

The carbon black (CB) applied was from the Xinxiang Deron Chemical Co., Ltd., China, and the main properties are listed in Table 1, especially with electrical resistivity lower than 0.43 Ω cm. The microstructure of the CB observed by scanning electron microscope (SEM) is shown in Fig. 1, illustrating the uniform dispersed CB particles. General Purpose Cement which was produced from Portland cement clinker and gypsum by Independent Cement & Lime Pty. Ltd., Australia, containing mineral additions up to 7.5%. Its physical and chemical properties are displayed in Table 2. Silica fume for partial substitution of cement was supplied from Concrete Waterproofing Manufacturing Pty. Ltd. (Australia). In the purpose of better carbon black dispersion, high range water reducer purchased from SIKA Australia Co., Ltd. was assisted. Specimens were cast using plastic cubic moulds with 50 mm in length, and the copper meshes with aperture of 2.68 mm were embedded as electrodes. Tap water in University of Technology Sydney (UTS) Tech Lab was used for the mix design.

Table 1
Physical properties of carbon black.

Particle size (nm)	Resistivity (Ω·cm)	Pour density (g/l)	DBP (ml/ 100 g)	Surface area (m^2/g)	pH value	Ash content (%)
20	<0.43	0.375	280	254	7.5	<0.3

2.2. Specimen preparation

Table 3 lists the mix proportion of CB filled cementitious composites. The specific fabrication process of CB filled cementitious composites is illustrated in Fig. 2, which includes the well-dispersed CB solution preparation and the mixing of CB/cement composites. There are 7 major steps for the manufacturing of piezoresistive CB/cement composite. Firstly, half of the water was added into the mixer, then gently poured in the water reducer and stirred for 5 min at low speed to avoid the formation of air bubble. Secondly, weighted CB was added into the solution, followed by another 5 min mixing. In this study, 3% CB particles to the weight of binder (cement and silica fume) were explored. Thirdly, slowly decant the rest water down a stirring rod to wash away the attached carbon black, then another 3 min stirring was needed. The mixing rate of second and third procedures was kept at a low speed, owing to the solution might splash out at high mixing rate. Fourthly, the well-dispersed CB solution is prepared for CB/cement composites. Fifthly, pour in the mixture of cement and silica fume, and firstly stirred at the low rate for 1 min, then switch to the high rate for another 3 min mixing. Sixthly, pour the mixture into the mould and insert copper meshes. Mechanical vibration is followed before placing the specimens into curing chamber. Finally, specimens were demolded after 1 day curing in the chamber, then moved to the curing chamber for another 28 days, with the controlled temperature at 20 ± 5 °C and relative humidity of 95%. After the manufacturing of CB filled cement-based composites, the specimens were heated/cooled to the specific temperatures, and dried/water immersed to reach the specific water content or subjected to the treatments of freeze-thaw cycles.

2.3. Various temperatures

The temperature equilibrium of the internal and external cement-based composite took approximately 4 hr for the cylinder with 50.8 mm in diameter and 101.6 mm for length [36]. In this study, the cubic specimens were film sealed to prevent the loss of water content and reduce any other variables affecting the results, while that might obstruct the heat exchange during oven heating. Therefore, the time span of specimens in oven with specific temperature was set slightly longer to 5 hr. Previous studies demonstrated that the ices generation of pore solution in concrete have resulted in resistivity changes because of volume expansion [35,38,39]. In order to further understand the effects of temperature changes, freeze-thaw cycles and ices generation on the resistance and piezoresistivity of CB cementitious composites, specimens which were only subject to one cycle of temperature increases from 5 °C, 20 °C, 40 °C, 60 °C, 80 °C and 100 °C, were prepared as control group to explore the temperature sensitivity. On the aspects of freeze-thaw treatment and ice generation, two groups of heating and cooling cycles were represented. The first one was higher than the

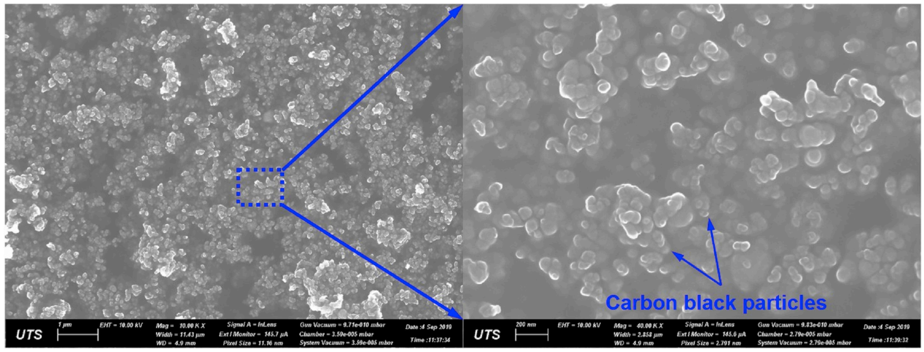


Fig. 1. Morphology of conductive carbon black particles.

Table 2
Physical and chemical properties of General Purpose cement.

Fineness Index (m^2/kg)	Initial setting time (hr)	Final setting time (hr)	Chloride (%)	Portland Clinker (%)	Gypsum (%)	Mineral addition (%)
370–430	1.5	3	0.01	85–94	5–7	Up to 7.5

Table 3
Mix proportions of carbon/cementitious composites.

Carbon black content	Cement	Silica fume	Tap water	Water reducer
3%*	0.8	0.2	0.45	0.8%

Note: Figures under the carbon black content, cement, silica fume, water and water reducer present their ratios to the weight of binder, e.g. 3%* under CB content presents the mass fraction of CB to the sum of cement and silica fume.

freezing point of water as 5 °C, 20 °C, 40 °C, 60 °C, 80 °C and 100 °C, and the second one was −20 °C, 5 °C, 20 °C, 40 °C, 60 °C, 80 °C and 100 °C. Each group experienced 10 cycles of heating and cooling treatments.

On the other hand, the heat exchange between the heated/frozen specimens and the ambient environment greatly affected both resistivity measurement and *FCR* during compression. To eliminate its impacts, the resistance measuring time was controlled less than 200 s, and the induced *FCR* due to the heat radiation or heat absorption in an ambient environment of 20 °C and 60% relative humidity should be removed. To obtain the relationship between *FCR* and the heat radiation in lab environment, the heated (under 100 °C) and the frozen (under −20 °C) CB filled cement-based composites were moved to the ambient environment without any treatments. The resistivity changes in the process of heat radiation or heat absorption were collected as the relationship between *FCR* to heat exchange.

2.4. Various water contents

Water content of CB cementitious composite was determined by the weight of totally dried specimens and that filled with evaporated water. The water content of composite is donated by:

$$w_c = \frac{m_w}{m_d} = \frac{m_c - m_d}{m_d} \tag{1}$$

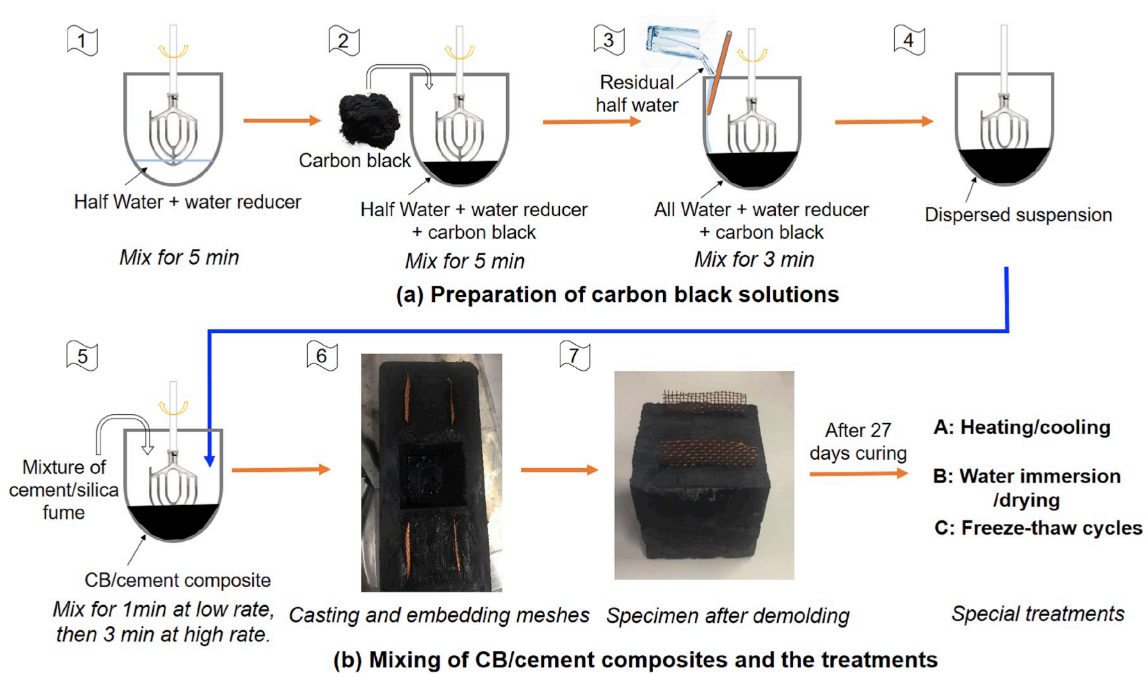


Fig. 2. Fabrication procedures of CB filled cementitious composites and the treatments after curing.

where w_c indicates water content of CB/cement composite; m_w represents the weight of evaporated water in composite; m_d is the weight of totally dried composite; m_c means the original weight of composite without any other treatment.

For the specimens with the same mixture ratio, manufacturing procedures, curing and drying environments, it can be assumed that they possess similar water contents in the dried and saturated status, respectively, among different individuals. To obtain the above listed variables, original weights of each specimen (m_c) are firstly recorded. Then the specimens were put in the oven with temperature of 60 °C for drying, and measured the weight every day, until the values keep constant to obtain the original water content. Afterwards, dry the CB/cement composite in different degrees, to obtain the exact water content ratios we needed. The specific specimens containing water content higher than w_o were water immerged in different degrees, and measured their weights in the condition of dry surface. Similarly, special film treatment on the specimens is carried out to prevent the humidity exchange of CB cementitious composites and the ambient environment, or the water loss during the heating process.

2.5. Piezoresistive behaviours

The piezoresistive behaviours of 3% CB cement-based sensor under different temperatures and water contents were experimentally investigated, by the cyclic compression at the stress magnitude of 2 MPa. Three cycles were carried out to evaluate the piezoresistive repeatability. Electrical resistance was measured through SIGLENT SDM3045X digital multimeter with acquiring rate of 5 figures per second. The electrical resistivity was calculated by the formula as follows:

$$\rho = RA/L \tag{2}$$

where R is the measured electrical resistance in ohm (Ω); A denotes the cross-sectional area of electrodes to specimens in squire meter (m^2); L represents the distance between two electrodes (m). The sensitivity was assessed by the value of gauge factor, which could be presented in Eq. (3):

$$GF = \frac{FCR}{\Delta\varepsilon} = \frac{\Delta\rho}{\rho_0 \Delta\varepsilon} \tag{3}$$

where GF denotes the gauge factor; FCR denotes the fractional changes of resistivity, which is the ratio of resistivity changes ($\Delta\rho$) to the original electrical resistivity (ρ_0); $\Delta\varepsilon$ is the changes of compressive strain during compression.

3. Results and discussion

To solve the problems of thermal radiation and absorption during compression test, the *FCR* of CB/cementitious composite exposed to the laboratory without any treatments was firstly obtained. Afterwards, based on the original *FCR* during cyclic compression and the *FCR* without treatments, the calibrated *FCR* could be obtained for the composites exposed to different temperatures. Afterwards, the results of different water contents on the piezoresistivity were represented and the potential conductivity mechanisms were proposed. Finally, the effects of freeze-thaw cycles on the resistivity and piezoresistivity were investigated.

3.1. Effect of temperature on piezoresistivity

3.1.1. Effect of thermal exchange

Fig. 3 illustrates the *FCR* variation of CB cementitious composites exposed in the ambient environment of 20 °C and 60% relative humidity without any external forces. It represented an opposite tendency among the heated and the frozen composites, with the increased resistivity by the heated specimens and the decreased resistivity by the frozen ones. Based on the theory of thermal exchange, this phenomenon is owing to their different exchange patterns. Since the composites under high temperature tended to emit heat into the ambient and decreased the temperature until reaching equilibrium, the resistivity of composite decreased gradually with the exposure time. On the contrary, the frozen composites had a trend to absorb heat from the ambient environment and increased the temperature to decrease their electrical resistivity.

Generally, curves of the relationship between *FCR* and exposure time from both thermal radiation and absorption of the CB/cementitious composite are in linear relationship, with the slope fluctuation as low as 10^{-5} in Fig. 3. After 15 min of air exposure, the *FCR* changes for the thermal absorption reached higher than 30%, while the values even higher for the composites under thermal radiation and achieved nearly 40%. The results are probably out of their different degree of temperature deviations to the room temperature, which reach at 80 °C for the heated composites (under 100 °C) and only 40 °C for the frozen ones (under −20 °C). In other words, the fractional changes of resistivity for the CB/cementitious composites are highly depended on the temperatures. Thus, unless the compression tests on these high/subzero temperature CB/cementitious composites were carried out in the incubator with identical environmental temperature, the *FCR* alterations induced by the thermal exchanges was not excluded in the next section of piezoresistive test on the CB/cementitious composites under various temperatures.

3.1.2. Piezoresistive properties at various temperatures

Under the loading regime of three cycles and the stress magnitude of 2 MPa as loading limit, Fig. 4 shows the *FCR* and strain development of composites at different temperatures of −20 °C, 20 °C, 60 °C and 100 °C. Generally it was observed that only the specimens at the room temperature of 20 °C exhibited excellent repeatability on electrical resistance, while all the other cementitious composites at the higher or lower temperatures performed gradual increase or decrease in the loading process and led to the irreversible *FCR* changes. Based on the aforementioned results, the original *FCR* changes (dotted red lines) were generated from the combined action of both cyclic compressive stress and the thermal exchange. Therefore, to eliminate the effect of thermal radiation and absorption on the irreversible resistivity of cementitious composites, the calibrated *FCR* (red lines) on the basis of the decreasing or increasing *FCR* of untreated specimens in the ambient environment were carried out. Overall, after the temperature calibration of *FCR* to remove the effect of thermal exchange, all the heated or frozen CB/

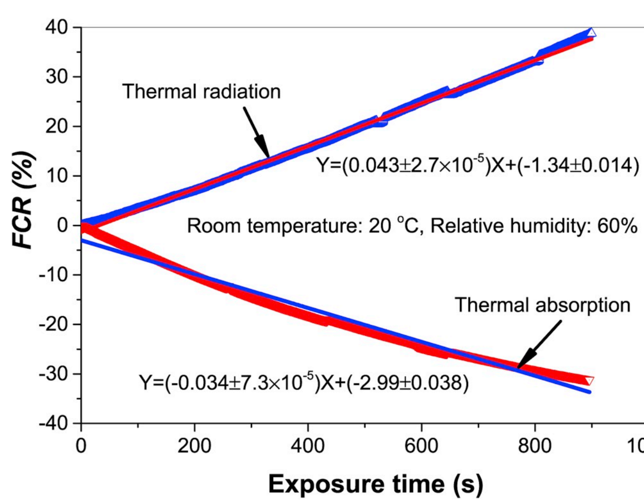


Fig. 3. Relationship between thermal radiation/absorption and *FCR* of dry CB cementitious composites under temperature of 20 °C and relative humidity of 60%.

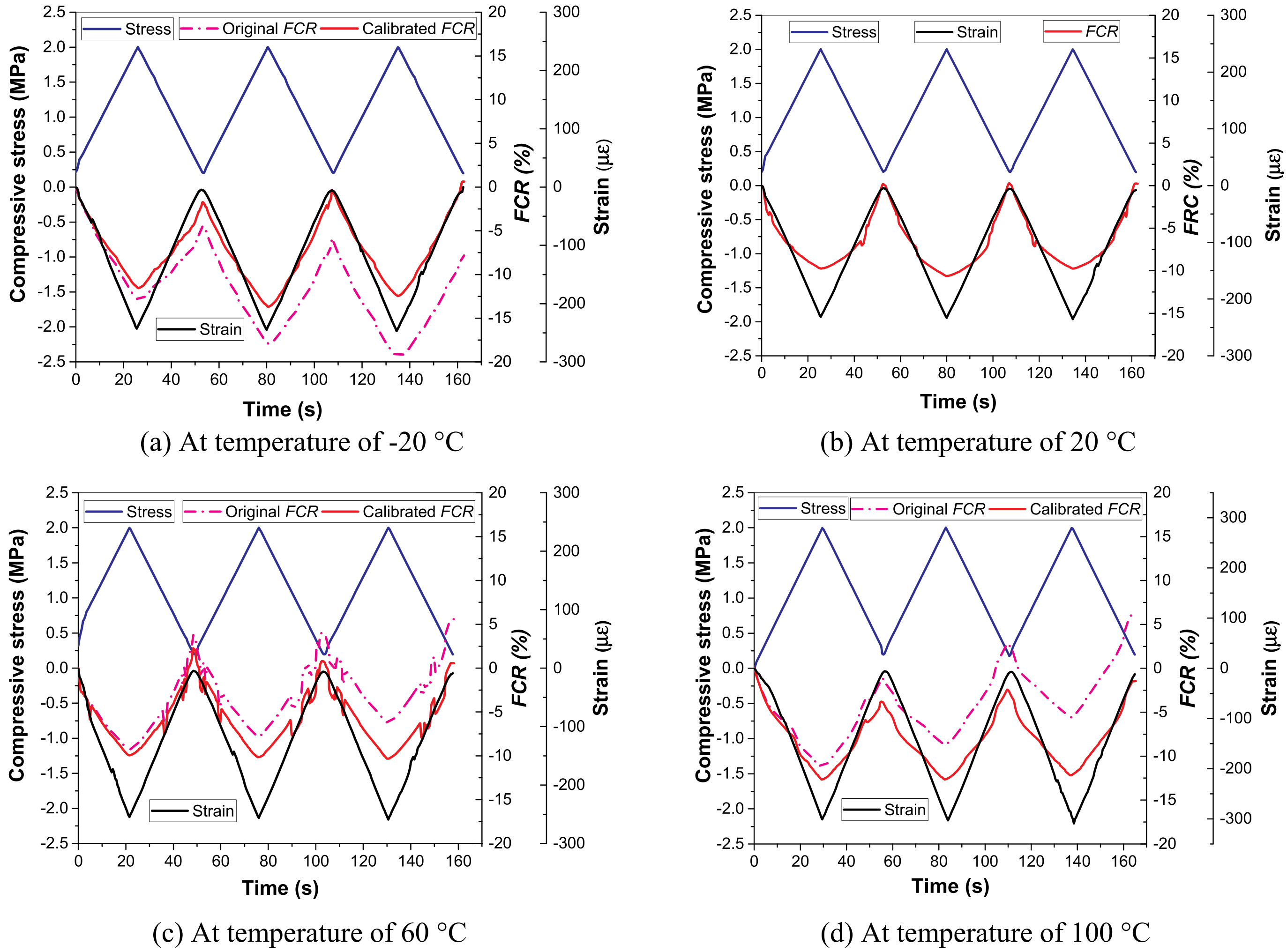


Fig. 4. The *FCR* of dry CB cementitious composite at different temperatures under cyclic compression.

cementitious composites showed good synchronicity and repeatability to compressive stress. The results illustrated that the temperatures themselves from −20 °C to 100 °C can't affect the repeatability of CB/cementitious composites. However, under the extreme circumstances with fire attacks, concrete infrastructures embedded with CB/cementitious sensors might undergo temperature higher than 450 °C. The repeatability of CB/cementitious composites is still unknown for the both reduced conductor content because of the oxidized carbon black particles and the damaged C–S–H gels [43].

In terms of the sensitivity of CB/cementitious composites under different temperatures, assessments were conducted through the *FCR* alterations by per unit strain which is also known as the gauge factor (see Eq. (3)). It indicates that during a loading process, both the changes of *FCR* and compressive strain are of importance to the sensitivity of cementitious composites. Fig. 5 compares the relationship between their strain and *FCR* changes among CB/cementitious composites at different temperatures. The composites under 100 °C were provided with largest *FCR* of 12.6% as well as producing the largest strain values. However, both smallest *FCR* changes and compressive strain were generated for the composites at the room temperature.

Even though there were small differences between composites at different temperatures, two sections could be divided according to the curves of *FCR* to strain. It seems that higher rate of fractional changes of resistivity occurred at low strain, while the resistivity change rate decreased when the compressive strain reached the limit of 30×10^{-6}. This is consistent to the investigations by Pang et al. [44] who proposed

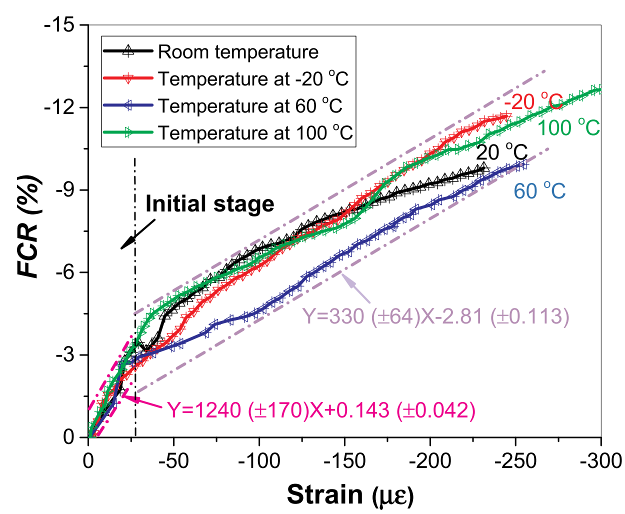


Fig. 5. Relationship between *FCR* and strain for CB cementitious composites under various temperatures.

that the reduced interfacial distance between conductive fillers and cement matrix was responsible for the swift resistivity alterations during initial loading. To describe their differences on the gauge factor and sensitivity, the fitting formulas of these curves in the two sections were plotted in Fig. 5. Their fitting errors were also followed in the formulas. It shows that in the initial loading stage, much higher gauge factor reaching 1240 was achieved, which demonstrates the ultra-high sensitivity of CB/cementitious sensor with small deformations. However, with the increase of strain, the increasing rate of *FCR* was greatly reduced and the gauge factor of approximately 330 was obtained. There are several potential reasons for the decreased gauge factor or sensitivity. The first reason is probably owing to the higher CB content and the excellent electrical conductivity of cementitious composites, where exists uneven CB agglomerations which could be connected and decrease the resistivity with very small deformations. The second is because of the minor pores in the CB/cementitious composites, where physical and electrical properties were nonlinear and vulnerable to the deformations, and led to the damaged microstructures and decreased gauge factor. Furthermore, as mentioned above, the sudden resistivity reduction was likely due to the easier reduced interfacial distance between CB particles to cement matrix [44].

The experimental results illustrate that both the repeatability and sensitivity of 3% CB filled cementitious composites makes no differences on account of different application temperatures from $-20\,^{\circ}$C to $100\,^{\circ}$C. However, the temperature changes or thermal exchange during the service of cement-based sensors affected its electrical characteristics and must be calibrated. In addition, the sensitivity was influenced by different loading stages, with the much higher sensitivity at the initial loading stage and the relatively lower but more stable sensitivity in the later loading stage.

3.2. Effect of water content on piezoresistivity

3.2.1. Piezoresistive properties at various water contents

Fig. 6 depicts the *FCR* and compressive strain changes of CB/cementitious composites at different water contents under the same cyclic compression. It was observed that the *FCR* changes showed excellent repeatability when the CB cementitious composites contained water contents lower than 12%, which was only accompanied with a small fluctuation on resistivity changes. Also, it represents that the CB/cementitious composites containing water content of 4% and 8% expressed larger *FCR* changes than that with 12% water content and the dry specimens. However, for the saturated specimens and the composites containing water content of 16%, it depicts that the composites not only showed lower *FCR* changes, but along with more volatile and fluctuated *FCR* alterations. One reason for these fluctuations is because of the polarization effect in pore solutions, where exists movements of ions in electric field until reaching electrical potential balance [45]. Another reason is that the water content affects the concentration and the number of solution filled pores, the touch and detach of nearby pore solutions also increased the curve volatility [31].

Fig. 7 displays the dependence of *FCR* to the compressive strain for cementitious composites with different water contents. It was observed that the sensitivity of CB/cementitious composites firstly increased and then decreased with rise of water content. For the composites at the saturation state, the piezoresistivity experienced the lowest sensitivity with the gauge factor of approximately 150. Then the gauge factor slightly increased to nearly 175 for the composites cooperating 16% water content. The composites at dry state and that with 12% water content showed nearly identical gauge factor of 400, with small discrepancy on the rapid growth in the early stage for the former and in the late stage for the latter. The rough evaluation of optimal water content for CB/cementitious composites was approximately at 8%, with the gauge factor reaching the value of 488. To acquire more precise optimum value of water content in the CB/cementitious composites, more tests are needed to narrow down the interval of water content in the composites.

In terms of the tendency of individual curve, it was seen that for the dry specimens and the composites with water content of 4% and 8%, their growth rates of *FCR* (gauge factor) gradually decreased with the loading process. However, for the composites at saturated state and that with 12% and 16% water content, their *FCR* growth rates were well maintained (saturated specimens and that with 16% water content) and even gradually increased (composites with 12% water content). This is probably out of the easier contact between CB particles without the interferences from water content, and the detailed explanation will be presented in the next section. In summary, the water content influenced both repeatability and sensitivity of CB/cementitious composites. Based on the current experimental results and previous studies [31], the potential mechanisms will be discussed in the next section.

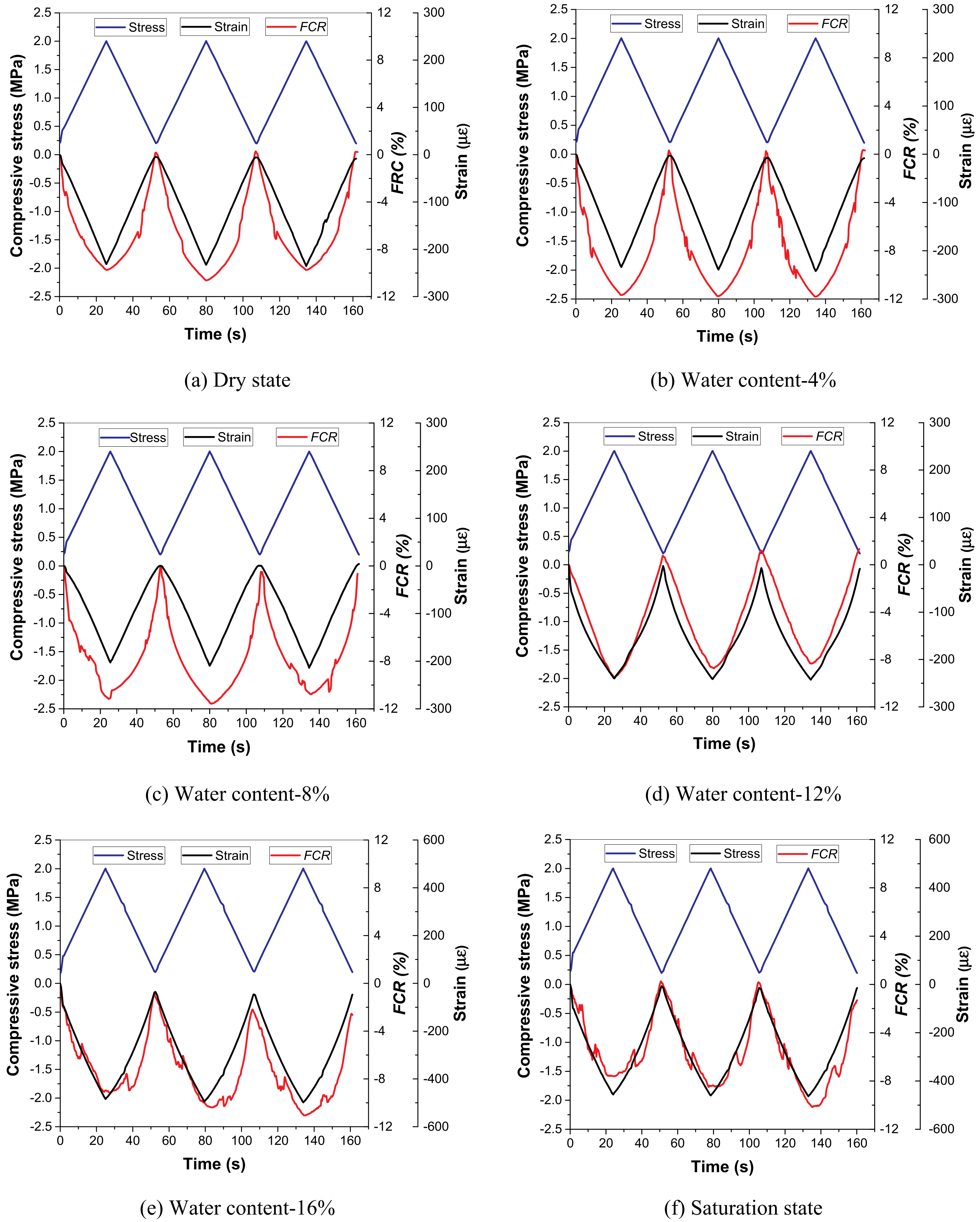
3.2.2. Mechanism discussion

As mentioned above, the increase of water content affects the sensitivity of CB cementitious composites, by firstly increasing then decreasing the gauge factor. Fig. 8 shows the electrical resistance changes of composites with different water contents, and relative positions between CB particles in different stages on account of water content, striving to explain the relationship between the CB particles, water content, electrical resistance and the aforementioned piezoresistivity. Different stages from *A* to *D* represent the dry stage, less-water stage, medium-water stage and the large-water stage, respectively. The CB particles enclosed by water layer demonstrated transformation among different conductive mechanisms, due to the increase of water content in the CB/cementitious composites. It was observed that the electrical resistance of cementitious composites increased with the water content, from approximately $102\,\Omega$ for the dry composites to nearly $620\,\Omega$ for the saturated ones. One possibility for the increased electrical resistance was due to the decreased conductivity of the water enclosed CB particles. Also, the higher water content resulted in severe polarization effect during the resistance measurement and caused larger measuring errors, especially for the cementitious composites under high temperatures [46].

It is widely known that the electrical conductivity includes electronic conductivity which is generated from the movement of free electrons, and the ionic conductivity that produced out of ions' movement [47]. In the dry stage (Fig. 8-A), the electrical conductivity mainly came from the contacts between CB particles, which possessed the electrical resistivity of lower than $0.43\,\Omega\,\mathrm{cm}$. It seems that the direct contact between CB particles could provide a very low resistance to the electrons' movement and improve the conductivity of cementitious composites. As for the piezoresistivity, the *FCR* changes were only due to the contact between CB particles to reduce electrical resistance, while the cement hydration products with worse conductivity rarely altered the resistance and the *FCR*.

With the increase of water content, the composites came to the less-water stage (Fig. 8-B), where some CB particles were enclosed by water layers. It blocked the direct connections among CB particles by thin water film to reduce the electrical conductivity. Interestingly, the piezoresistivity in this stage was improved, just like the composites with 4% and 8% water content, respectively. This is because the *FCR* changes were not only due to the contact of CB particles, there also were resistance reduction because of the ions movements such as Ca^{2+}, OH^- and SO_4^{2-} in the water layers [34]. Owing to the limited water content, most of the *FCR* changes still came from the CB particles, and brought the largest gauge factors.

The followed medium-water stage (Fig. 8-C) exhibited higher electrical resistance just as the composites with 12% and 16% water content. In this stage, increased CB particles were covered by the water layers, which considerably increased the contact resistance between CB particles. Although the *FCR* changes from the ions conductivity was stimulated, the electrical responses from the contact of CB particles were weakened due to the water layer decreased conductivity. According to the reduced gauge factor, it was deduced that the negative effect on the electronic conductivity of CB particles and the induced piezoresistivity overwhelmed the positive effect brought by water content introduced ionic conductivity.



(a) Dry state

(b) Water content-4%

(c) Water content-8%

(d) Water content-12%

(e) Water content-16%

(f) Saturation state

Fig. 6. The *FCR* of CB cementitious composites with different water contents under cyclic compression.

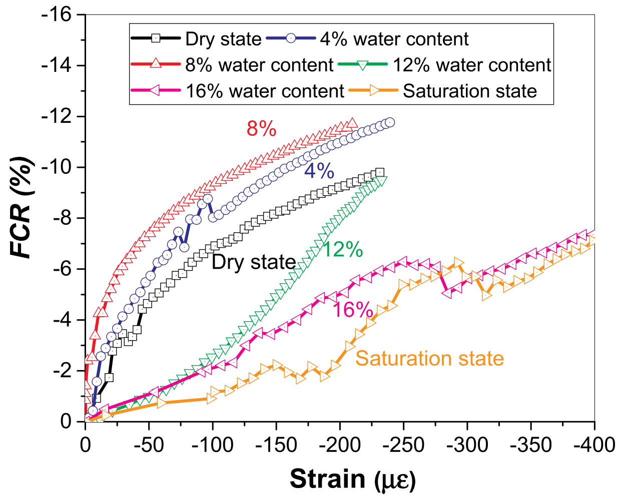


Fig. 7. The *FCR* of CB cementitious composites at different water contents as a function of compressive strain.

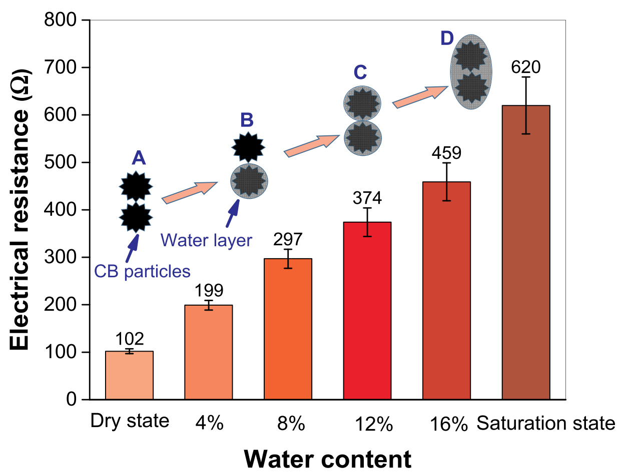


Fig. 8. Resistance of CB cementitious composites to water content and the relative positions between CB particles on account of water layers.

In the case of saturated cementitious composites, it was found from Fig. 8-D that the CB particles or small CB agglomeration were entirely surrounded by water layers. In this circumstance, the ions conductivity had predominance on the electrical conductivity than the electrons conductivity and led to highest electrical resistivity [31]. Since the CB particles totally inside the water layers, the applied load firstly caused the deformation of composites and then delivered to the deformation of water layers, and finally transmitted to the location alterations of CB particles. As plotted that the saturated composites and the composites with water content of 12% and 16% had lower gauge factor at the initial loading stage and relatively higher gauge factor in the later stage, just because the *FCR* changes were firstly induced by ion conductivity, and then produced by the electrons conductivity. Even if the *FCR* changed by water layers increased, it greatly decreased the *FCR* changes by the contact of CB particles, and then reduced the whole sensitivity. Moreover, the intensity of ionic conductivity mainly depended on the ion concentration of pore solutions and water layers, which was hardly altered during the compression process and failed to significantly improve the *FCR* changes and piezoresistivity.

3.3. Effect of freeze-thaw cycles on piezoresistivity

Results show that the water content played a vital role in the process of freeze-thaw treatment, since the freezing water expanded its volume which might cause inner stress inside the CB/cementitious composites to damage the microstructures and influence the electrical resistivity [35, 48]. Therefore in this section, the totally dried and saturated specimens were prepared to investigate their electrical resistivity and piezoresistivity under the effect of freeze-thaw cycles. Different from other studies to apply the temperatures from −20 °C to 20 °C [39] or −20 °C–52 °C [38], the chosen temperatures for freeze-thaw cycles are from −20 °C to 100 °C, to more closely imitate the environmental conditions where the cementitious composites might receive higher temperature when long-term exposure to intensive sunshine weather.

3.3.1. Resistivity development under different cycles

Fig. 9 illustrates the resistance changes of dry CB/cementitious composites in two patterns of heating and cooling cycles. The small diagram at top right is the heating and cooling process without water freezing, and the larger one involves the subzero temperatures called the freeze-thaw cycles. Both patterns included 10 cycles of heating and cooling process. It was found that only a small discrepancy were observed among electrical resistances in different cycles at the same temperature, and showed good repeatability even in the process of freeze-thaw cycles. For the dry specimens without free water, the resistance changes of CB/cementitious composites under various temperatures mainly came from the bound water [49]. It could be altered in viscosity and ionic activity of solutions with temperatures to change the electrical resistance of cementitious composites. However, the bound water can't be eliminated under the drying condition of 100 °C [50], hence it can be deduced that the resistance repeatability of dry CB/cementitious composites are immune from the freeze-thaw cycles, regardless of the heating and cooling processes with or without the freezing stage. This phenomenon is easy to understand for the lack of free water which fails to get frozen and expand its volume to damage the microstructures of cementitious composites.

Fig. 10 shows the resistance development of CB/cementitious composites under the same treatment of heating and cooling patterns in the saturation state. Compared to that of dry specimens, the electrical resistance of saturated cementitious composites were more sensitive to the temperature changes, because of a great amount of free water in the composites. The resistance drops with increase of temperature were partially due to the worse viscosity of solution resistance, while the main reason is because of the activated ions in the pore solution to greatly reduce the electrical resistance [51]. For the cycles without the subzero temperature, small divergence on the resistance was measured at the same temperature and showed good repeatability. In comparison to the similar results from the dry specimens, the deduction could be proposed

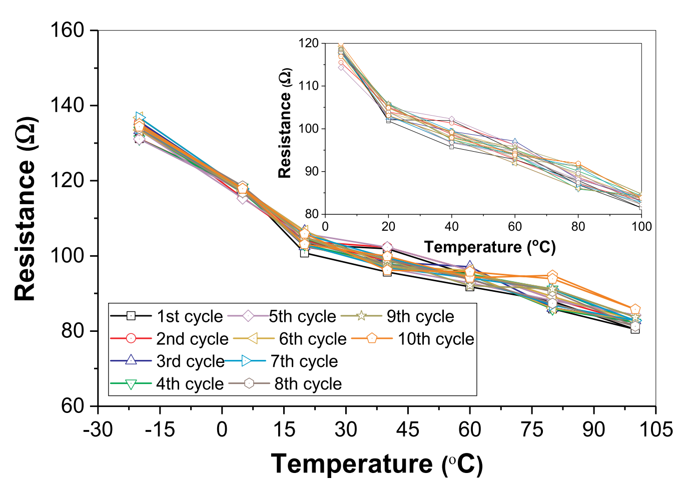


Fig. 9. Electrical resistance development of dry CB cementitious composites with or without subzero temperature exposures.

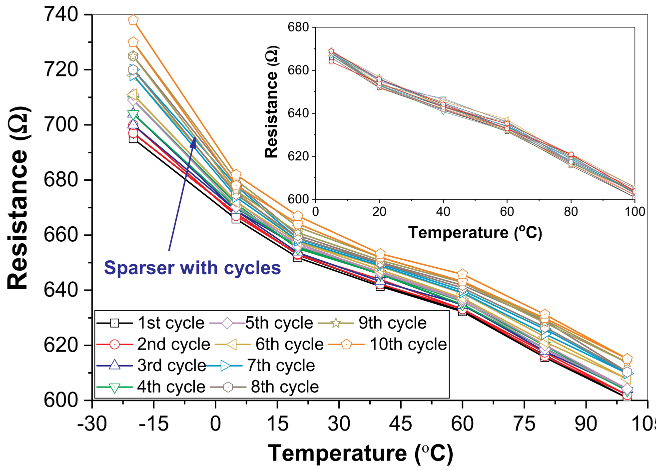


Fig. 10. Electrical resistance development of saturated CB cementitious composites with or without subzero temperature exposures.

that the temperature cycles above the zero had no impacts on the electrical resistance of CB/cementitious composites, no matter how much water content they contained. In terms of the freeze-thaw cycles on the saturated specimens, an obvious larger resistance discrepancy was generated with the increase of freeze-thaw cycles, especially the resistance of composites at the temperature of −20 °C. This can be explained by the effect of water freezing and expansion on the micro conductive network in the CB/cementitious composites, which might be permanently destroyed and result in higher resistance with freeze-thaw cycles.

3.3.2. Piezoresistive properties after freeze-thaw cycles

Fig. 11 illustrates the changes of compressive strain and *FCR* before and after 10 cycles of freeze-thaw treatment for the dry CB/cementitious composites under the same cyclic compression. The dotted lines are the results before the freeze-thaw cycles and the solid lines represent the same composites after the freeze-thaw cycles. It was observed that the composites before the freeze-thaw cycles exhibited excellent repeatability and sensitivity with compressive strain, while for the composites after the freeze-thaw cycles, slightly higher *FCR* were observed in the second cycle and a bit lower *FCR* were occurred in the first and third cycle. The average of largest *FCR* was similar before and after freeze-thaw cycles, and the small discrepancy could be attributed to the minor differences in microstructures between composites. Hence, it could be considered that the freeze-thaw cycles made no differences on the electrical resistivity of the dry CB cementitious composite, which was consistent well with the repeatable resistance in Fig. 9. On the other hand, as for the compressive strain of CB/cementitious composites, higher deformation by compression was observed after the freeze-thaw cycles, with the ultimate strain increasing by approximately 11.9%. As a result, the sensitivity parameter of gauge factor was decreased owing to the maintained *FCR* values but the increased strain. Generally, the piezoresistive repeatability of the dry CB cementitious composites was well preserved with gentle fluctuation after the freeze-thaw cycles. As the piezoresistive sensitivity depended on the both electrical and mechanical properties, and freeze-thaw cycles might weaken the mechanical properties of composites by enlarging the compressive strain [52], the dry CB/cementitious composites still expressed a reduced gauge factor by a rough approximation of 11.9% (equal to the increased strain) after the freeze-thaw cycles.

In the aspect of saturated CB/cementitious composites, their *FCR* and compressive strain changes before and after the freeze-thaw cycles were more complicated than that of dry CB/cementitious composites, since the volume expansion of pore solutions generated stress concentration and damaged the microstructures of composites. As mentioned before that the saturated CB/cementitious composites without freeze-thaw cycles could provide the relatively high *FCR* but with worse linearity and repeatability, just as the pink dotted line in Fig. 12. However, after the treatment of freeze-thaw cycles, much more significant fluctuations on the resistivity output and the lower *FCR* could be observed for the saturated CB cementitious composites. The aforementioned reasons for the resistivity fluctuations were mainly due to the impacts by the connection of pore solutions, however, in this section, the extreme volatility was not only attributed to the interferences by pore solutions, but was determined by the microstructural damages of cement matrix, which might establish the conductive passages again in cementitious composites and greatly affect the electrical resistivity. As for the reasons for the decreased peak values of *FCR*, the elastic part of the microstructures in cementitious composites which brought about the repeat resistivity in a cyclic compression was vulnerable and limited. The freeze-thaw cycles induced stress concentration inside the composites could permanently destroyed the microstructures and caused lower resistivity changes of the cementitious composites. Furthermore, the compressive strain of the saturated CB/cementitious composite was slightly larger than that of dry specimens which increased by 14.6%. In the case of the second compressive cycle that possessed relatively smooth *FCR* changes to evaluate the sensitivity reduction, the gauge

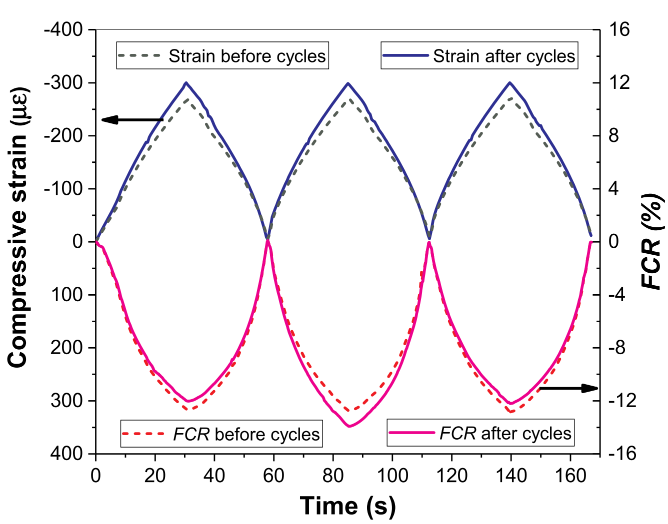


Fig. 11. The *FCR* changes of dry CB cementitious composites with compressive strain before and after the freeze-thaw cycles.

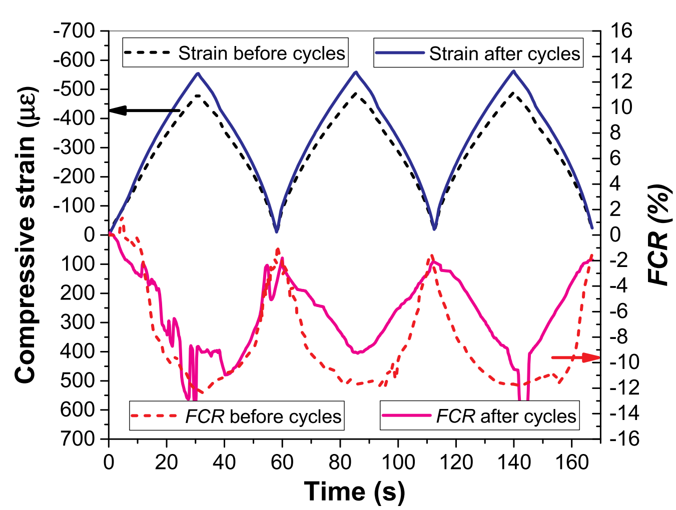


Fig. 12. The *FCR* changes of saturated CB cementitious composites with compressive strain before and after the freeze-thaw cycles.

factor for saturated CB/cementitious composite after the freeze-thaw cycles dropped by approximately 30.7%.

Both the dry and saturated CB/cementitious composites showed weakened piezoresistive properties after the freeze-thaw cycles, because of the either increased compressive strain or the decreased *FCR*. The dry CB/cementitious composites possessed better resistance to the freeze-thaw cycles by smaller variations on the electrical resistivity, while the saturated CB/cementitious composites were sensitive to the freeze-thaw cycles due to the damages caused by volume shrinkage and expansion of pore solution. Overall, it demonstrated that the CB/cementitious sensors have limitations on the real applications in the environment with subzero temperatures, since the relatively weak mechanical properties and the poor frost resistance of CB particles.

4. Conclusions

The effects of various environmental factors, including the ambient temperatures ranging from $-20\,^{\circ}\mathrm{C}$ to $100\,^{\circ}\mathrm{C}$, the water contents from complete dry to saturation, and the freeze-thaw cycles on the electrical resistivity and piezoresistivity of CB/cement-based sensors were investigated in this study. The main conclusions can be draw up as follows:

(1) The *FCR* of CB/cement-based sensors greatly varied if there were extreme temperature differences between the sensors and working environments, due to the severe thermal exchanges. Therefore, the real application of CB/cementitious composites should be accompanied by a temperature compensation circuit or other special treatments for thermal insulation.
(2) After removing the heat exchanges interference, the piezoresistive properties of CB/cementitious composites were independent from the temperature variations ranging from $-20\,^{\circ}\mathrm{C}$ to $100\,^{\circ}\mathrm{C}$, and showed both satisfactory sensitivity and repeatability of piezoresistivity.
(3) With the increase of water content, in addition to the increased electrical resistivity, the piezoresistive sensitivity of CB/cementitious composites firstly increased but then decreased, and the optimal water content was found out around 8%. Moreover, the high water content in the cementitious composites could make the resistivity behaviours fluctuate widely.
(4) The freeze-thaw cycles exhibited limited impacts on the electrical resistivity of dry CB/cementitious composites, but the induced higher compression strain still caused reduced gauge factor and slightly lower piezoresistive sensitivity with reduction of 11.9%. However, both the electrical and mechanical properties of saturated CB/cementitious composites were greatly affected by the freeze-thaw cycles, which resulted in the decreased piezoresistive sensitivity by 30.7%.

Acknowledgements

All the authors appreciate the financial supports from the Australian Research Council (ARC) (DE150101751), University of Technology Sydney Research Academic Program at Tech Lab (UTS RAPT), University of Technology Sydney Tech Lab Blue Sky Research Scheme and ARC Industrial Transformation Research Hub Component Project "Nano-geopolymer composites for underground prefabricated structures" collaborating with Wuhan Zhihe Geotechnical Engineering Co., Ltd.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2019.107488.

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